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Keywords

Dimethyl disulfide, Emissions, Mortality compost, SPME, VOCs

Disciplines

Agriculture | Animal Sciences | Bioresource and Agricultural Engineering | Environmental Sciences

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Abstract

Biosecure livestock mortality composting systems have been used to dispose of diseased livestock mortalities. In those types of system, visual inspection of carcass degradation is not possible and monitoring VOCs (volatile organic compounds) released by carcasses is a new approach to assess progress of the composting process. In this study, field-scale livestock mortality composting systems were simulated and a laboratory scale composting system with aerobic and anaerobic test units was designed to collect VOC samples from the headspace of decaying plant materials (70 grams dry weight) and swine tissues (70 grams dry weight) at controlled operating temperatures. Headspace samples were collected with SPME (solid phase microextraction) and analyzed by a GC-MS (gas chromatography – mass spectrometry) system. Among the 43 VOCs identified, dimethyl disulfide, dimethyl trisulfide, and pyrimidine were found to be marker compounds of the mortality composting process. These compounds were only found to be produced by decaying swine tissues but not produced by decaying plant materials. The highest marker VOC emissions were measured during the first three weeks, and VOCs were not detected after the 6th week of the process, which indicates degradation processes were completed and compost materials microbially stabilized (no additional VOC production). Results of respiration tests also showed that compost materials were stabilized. Results of this study can be useful for field-scale composting operations but more studies are needed to show the effects of size and aeration rate of the composting units.

Keywords: Dimethyl disulfide; Emissions; Mortality compost; SPME; VOCs

1. Introduction

The safe disposal of carcasses during emergency animal disease (EAD) outbreaks is a significant issue since diseases can be easily spread to humans and other livestock (Wilkinson, 2007). Improper disposal of carcasses, such as illegal dumping, has become a problem due to cost of mortality disposal and limited number of licensed landfills, incineration and rendering services (Bonhotal et al., 2002). Biosecurity agencies in USA, Canada, Australia, and New Zealand have recognized the potential benefits of composting for emergency management of livestock mortalities (Wilkinson et al., 2007). Composting of diseased mortalities was first developed for the poultry industry (Spencer et al., 2004; Bendfeldt et al., 2006) with more recent studies being conducted to adapt mortality composting for swine and cattle emergency disposal (Glanville et al., 2006a, 2006b; Glanville et al., 2007; Ahn et al., 2007)

In case emergency disposal is necessary, a passively-aerated plastic wrapped mortality composting system has been designed to reduce the potential of spreading live viruses to the environment (Spencer et al., 2004; Ahn et al., 2007; Glanville et al., 2007). In this type of biosecure composting application, carcasses are fully covered with envelope (typically silage, straw, or hay) materials and the entire matrix is wrapped with plastic sheets. It is not safe to turn, mix, or expose the diseased carcasses to the environment until carcass degradation is completed, temperatures have been reached and maintained to inactivate pathogens, and compost is considered stable (Wilkinson, 2007). Since visual inspection of the carcasses is not possible, a new method is needed to assess progress and completion of the degradation process without compromising biosecurity. Temperature is

the most commonly used parameter for assessing performance of a composting process. However, monitoring temperature profiles does not necessarily help to evaluate progress and completion of the process. Reasons for low core compost temperatures may be over-aeration of the composting units and low heat retention properties of the envelope materials (Ahn et al., 2007; Glanville et al., 2007). Under these conditions, temperature may not increase but the degradation process can still continue. A new approach is to monitor VOCs (volatile organic compounds) released by decaying mortalities inside biosecure compost units (Akdeniz et al., 2009).

Volatile organic compounds emitted from composting of various wastes include a wide group of organic compounds, including sulfur-containing compounds, nitrogen-containing compounds, alcohols, phenols, ketones, esters, volatile fatty acids, and terpenes (Pagans, et al., 2006). Typically, VOCs are found in low concentrations (pg/L to µg/L) in the headspace of composting units. Sample preparation for VOCs in headspace requires pre-concentration (Dewulf and Van Langenhove, 2002; Clemitshaw et al., 2004). Ultraviolet differential absorption spectroscopy (UV-DOAS), Fourier transform infrared spectroscopy (FT-IR), and colorimetric sensors are the techniques that allow measurement of VOCs in headspace without sample preparation but the number of analytes that can be detected is limited (Lin et al., 2004). Gas phase SPME (solid phase microextraction) coupled with GC-MS (gas chromatography-mass spectrometry) based analyses is a more convenient (does not require sample preparation) method for measurement of VOCs in air and headspace (Koziel et al., 1999; Koziel and Novak, 2002). Solid phase microextraction has been used to sample VOCs from biofilter-treated effluent air of swine barns (Chen et al.,

2008), landfills (Davoli et al., 2003; Kim et al., 2005a), commercial composts (Kim et al., 2005b) and decaying plant and animal materials (Akdeniz et al., 2007a, 2007b).

There are many variables affecting analytical method development and quantification with SPME. One of the factors affecting air sampling with a SPME fiber is air temperature. Although there are more compounds in the vapor phase when the temperature increases, amounts of volatiles adsorbed can decrease (Jia et al., 1998; Demyttenaere et al., 2003). This can be explained by the fact that adsorption is an exothermic and competitive process (Pawliszyn, 1997). In addition, adsorption induces heat release, which can increase the temperature of the adsorbent and decrease the amounts of analyte adsorbed (Nongonierma et al., 2006).

In this study, a laboratory scale composting system, which simulated a field-scale biosecure composting systems was designed, built and tested to specifically monitor VOC emissions. Several operating variables were controlled, (i.e., composting time, temperature, and aeration flow rate resulting) in aerobic or anaerobic conditions. The objectives of the study were (a) to identify and compare VOCs evolved from decaying swine tissues and plant materials in order to find marker compounds of decaying swine tissues, (b) to develop air sampling and analyses methods for different air temperatures to accurately quantify marker VOC emissions, and (c) to evaluate a potential usage of VOC emissions to test completion of carcass degradation.

2. Methods

Compost test units were designed, prepared, and run in triplicate to identify and compare VOCs evolved from decaying plant and animal materials. These tests included

separate plant and animal material compost units and layered (plant-animal material) compost units (n=3 for each treatment). The separate units consisted of corn silage, oat straw, and alfalfa hay, and swine tissues (70 dry grams) composted separately at aerobic and anaerobic conditions (total of 24 units). The layered compost tissues consisted of combinations of corn silage and swine tissues (70 dry grams total), composted under aerobic and anaerobic conditions (total of 6 units). Corn silage was chosen for this combination because it emitted a higher number of VOCs among all plant materials tested (Akdeniz et al., 2007a).

2.1. Aerobic and anaerobic test units

Two oilless pumps (Combined Fluid Products, Lake Zurich, IL) were used to aerate aerobic test units. Air was pumped through hydrocarbon traps (Supelco, Bellefonte, PA) to prevent any VOC contamination from the ambient air. Curved PTFE tubing with equal number of holes were used to aerate test units (Fig. 1a). Air flow rate was set at 100 ± 1.66 mL/min by using stainless steel 3-way needle valves (Swagelok, Omaha, NE). As Rynk et al. (1992) suggested airflow rates of 707.7 to 2,831 L/min per dry tonne of compost were required for aerobic composting, we chose an air flow rate of 1.42 mL/min per dry gram (1,420 L/min per dry ton-average of 707.7 and 2,831 L/min per dry ton) and kept constant in all test units. Air flow rate of each test unit was set at 100 ± 2 mL/min and checked weekly from the outlet port of the test units (Fig. 1a). One hour before headspace VOC sampling, aeration was stopped and aerobic test units were kept closed to let the VOCs reach equilibrium in the headspace.

Humidified air was pumped through aerobic test units. Relative humidity at the outlet of the test units was calculated by measuring dry and wet bulb temperatures. Outlet of the test units were connected to small glass jars and dry/wet bulb temperatures were measured inside these jars using thermocouples (Omega Engineering, Stamford, CT). Wetted gauze was used to measure wet bulb temperatures (Fig. 1a). A datalogger (Model CR10X, Campbell Scientific, Logan, UT) was utilized to record temperature.

Anaerobic conditions were maintained by tightly closing the test units. Pure N₂ (99.995 % pure; Chemistry Store, Iowa State University) was passed through the test units for two minutes once a week to make O₂ and CO₂ measurements. Mass flow rate of N₂ was set at 1 L/min and checked by a mass flow controller (DryCal, Butler, NJ). Oxygen and CO₂ concentration measurements were completed immediately after VOC sampling. The O₂ trap (Alltech Associates, Chicago, IL) was used on N₂ delivery line to prevent any O₂ contamination and compromising anaerobic conditions.

2.2. Sample preparation and composting conditions

Plant materials (corn silage, oat straw, and alfalfa hay) were collected from central Iowa. Oat straw and alfalfa hay were chopped to approximately 10 cm lengths to prevent formation of an excessively porous structure. A whole swine carcass (6.3 kg, one month old), including bones, internal organs, and skin, was shredded using an industrial grinder in order to get a representative 70 g sample of the entire carcass. The initial moisture contents of the corn silage, oat straw, alfalfa hay, and swine tissues were 43.6, 37.7, 44.2, and 65.0 %, respectively. Moisture contents of the plant materials were adjusted to 65 % by

spraying deionized water and incubated at 30 °C for 24 h (Ahn et al., 2005). Moisture loss during incubation was calculated from weight change and added (sprayed) back.

Each separate test unit consisted of approximately 70 dry grams of plant and animal materials placed inside 0.946 L glass jars (Mason, Wal-Mart, Ames, IA) (Figs. 1a and b). Layered plant-animal material units simulated biosecure field-scale mortality composting conditions where plant and animal materials are layered and decayed together (Ahn et al., 2007; Glanville et al., 2007). In these test units, plant and animal materials were layered at the ratio of 1 (animal):15 (plant) (w/w) (70 dry grams total). This ratio was chosen based on previous field-scale biosecure composting experiments (Ahn et al., 2007; Glanville et al., 2007).

Glass jars that were used to compost plant and animal materials (Figs. 1a and b) were first washed with deionized water and heated at 110 °C overnight to drive off volatile impurities. Polytetrafluoroethylene (PTFE) liners with 0.8 mm thickness (USP, Lima, OH) were placed on the lids (inner side) to separate headspace of the jars from tin lids and to minimize interfering compounds from tin lids and seals. Sampling ports for SPME insertion and VOC collection were made by drilling 5 mm holes in the middle of the lids. Thermogreen half-hole septa (Supelco, Bellefonte, PA) were tightly placed in these holes. Air handling system was assembled from clean 6.35 mm O.D. Teflon (PTFE) tubing (E&S Technologies, Chelmsford, MA) and stainless steel fittings (Swagelok, Omaha, NE) to prevent any VOC contamination. All the test units were placed in water baths (Fisher Scientific, Chicago, IL). Temperatures of the water baths were adjusted every day manually (Fig. 2). Temperatures were increased up to 67 °C and then decreased to 22 °C during the first 8 weeks. This temperature profile was based on the average core temperature of a

warm season field-scale biosecure swine mortality composting process (Ahn et al., 2007; Glanville et al., 2007). After temperature decreased to 22 °C, it was increased again (Fig. 2) to check the potential for VOC emissions caused solely by temperature increase after the composting process is completed. This was done to determine if the biological activity had fully ceased during the composting period and compost materials were fully stabilized.

2.3 CO₂ and O₂ measurements

The headspace CO₂ and O₂ concentrations were measured on weekly basis from the outlet of the test units using a CO₂ (Vaisala, Louisville, CO) and O₂ (Apogee, Logan, UT) probe. The CO₂ and O₂ concentrations in the aerobic test units were recorded to test aeration status of the test units. Oxygen concentrations of anaerobic test units were measured in order to check for possible O₂ contamination. Carbon dioxide and O₂ probes were calibrated weekly using clean ambient air and gas mixtures (5% CO₂-15 % O₂ and 15 % CO₂-5 % O₂) prepared by the Chemistry Store, Iowa State University, Ames, IA.

2.4 Headspace SPME and GC-MS analysis

An 85 µm Carboxen/polydimethylsiloxane (CAR/PDMS) SPME fiber and 1 h extraction time was used to collect VOCs from the headspace of the test units. This SPME fiber and extraction time was chosen based on air sampling and analysis method development and optimization described elsewhere (Akdeniz et al., 2009). Samples were run using a 6890N GC and 5975 MS (Agilent Inc., DE). Pure helium (99.995 %) was used as the carrier gas at constant flow (1.7 m/s). The injector and SPME fiber desorption temperature was 240 °C. The initial temperatures of the GC oven were 40 °C with 3 min

holding time, followed by a ramp of 8 °C/min until reaching 220 °C, where it was held for 10 min. A polar capillary column (BP-21, 60 m × 0.32 mm ID × 0.25 µm film thickness, SGE, Austin, TX) was used to separate VOCs. The MS mass/charge (m/z) ratio was set between 29 and 150 for the first 8 min. After that, MS detection was between 34 and 280 m/z. The transfer line, quadrupole, and MS source temperatures were 240, 150, and 230 °C, respectively. Chromatography data acquisition software including MSD ChemStation (Agilent, New Castle, DE) and BenchTop/PBM™ V. 3.2.4 (Palisade Corporation, Ithaca, NY) were used to analyze data. Separated compounds were identified using mass spectral matches with ChemStation's NIST MS Library and PBM Benchtop MS libraries. Spectral matches and column retention times were compared with those of standard VOCs (Sigma-Aldrich, Milwaukee, WI).

2.5 Emission rate measurements

Calibration curves for air sampling and analysis were prepared using the methodology developed by Akdeniz et al. (2009). These authors reported that there was no significant difference between dry (0% relative humidity) and humid conditions (97% relative humidity) in extraction efficiency for dimethyl disulfide, dimethyl trisulfide, and pyrimidine. Therefore, calibration curves were prepared for only dry conditions. In this study, to simulate a field-scale composting process, temperatures of the test units were changed on daily basis (Fig. 2) and headspace VOCs were extracted at different temperatures. Thus, calibration curves were prepared at 20, 30, 40, 50, and 60 °C, respectively, to quantify MS detector response at different temperatures. First, standard gases of marker compounds were generated and collected inside glass sampling bulbs as

described in Akdeniz et al. (2009) and then they were subsequently placed inside an oven (The Grieve Corporation, Round Lake, IL) with a temperature controller. Glass bulbs were kept inside the oven for 10 min and headspaces were sampled for 1 h with 85 µm CAR/PDMS SPME fiber. Concentrations of the compounds were calculated using the calibration curve with the closest temperature to the sampling temperature. Emission rates of the marker compounds were calculated based on the following equation (Xin, 2005):

$$ER = Q * C * \frac{W_m}{V_m} * \frac{T_{std}}{T_a} * \frac{P_a}{P_{std}}$$

ER is the emission rate (µg/min), Q is the air flow rate (L/min), C is the concentration of the analyte (ppmv), W_m is the molecular weight of the analyte (g/mol), V_m is the molar volume of the analyte at STP (L/mol), T_{std} is the standard temperature (273.15 K), T_a is the ambient temperature (K), P_{std} is the standard pressure (101.325 kPa), and P_a is the ambient pressure (kPa).

2.6 Respiration rate measurements

Compost materials were incubated for nine weeks and after nine weeks 20 g of samples were collected from each unit and respiration rates of the remaining compost materials were measured. A titration method was used to measure the CO₂ production during respiration of remaining carcass tissues (Sadaka et al., 2006). For respiration rate calculations, moisture content was determined by drying samples at 105 °C for 24 h. Volatile solid contents of samples were measured by combusting dried samples at 550 °C for 5 hrs (APHA, 1989). Sadaka et al. (2006) adjusted moisture contents of compost

samples to 50% (w.b) but in this study moisture contents of the samples were increased to 65% since it was the initial moisture content of the swine tissues.

2.6 Statistical analysis

Experiments were run in triplicate (n=3). Statistical JMP v 6.0.2 package was used for data analysis. Data were subjected to one-way analysis of variance (ANOVA). Treatment means were compared using TUKEY's honestly significant differences (HSD) test at 95 % confidence level ($p \leq 0.05$ and $n=3$).

3. Results and discussion

3.1 Aeration and moisture supply

Oxygen and CO₂ concentrations in aerobic test units were found to be same as those in ambient air (0.03 % CO₂, 20.94 % O₂). The O₂ concentrations in anaerobic test units were always measured as zero. The CO₂ concentrations in anaerobic test units were lower than ambient air and ranged from 0.01 to 0.012 %. The results demonstrate that there was no limitation in O₂ supply to aerobic test units and no O₂ contamination to anaerobic test units. Moisture contents of the corn silage, oat straw, alfalfa hay, and swine tissues decreased to 29.1±1.01, 31.1±1.25, 32.0±0.98, and 32.2±1.21 %, respectively, at the end of the study (Table 3). The optimum initial moisture content of the compost materials is in the range of 40 to 60% (Haug, 1993). In this study, the initial moisture contents of the plant materials were increased to 65% (to approximate moisture content of the swine tissues) and during the process moisture contents of the plant materials and swine tissues decreased to approximately 30%. Final moisture contents can vary from 21% to 77% (Glanville, et al.,

2007) depending on the initial moisture content and the progress of the process. It is known that lowest moisture content at which bacterial activity takes place is from 12 to 15% (Shammas and Wang, 2007). In this study the final moisture contents were above 15% and it can be concluded that aerobic test units were humidified properly and over-drying of the compost materials due to excessive aeration was prevented.

3.2 Identification of marker VOCs

Forty three compounds including volatile fatty acids, esters, nitrogen-containing compounds, alcohols, phenols, ketones, sulfur-containing compounds and terpenes were identified in the headspace of corn silage, oat straw, alfalfa hay and swine composts (Table 1). Retention time and spectra of the compounds were matched with those of pure standards.

Among the forty three compounds, only three compounds were found to be evolved exclusively by decaying swine tissues, and were not produced by any of the plant materials tested. These marker compounds were dimethyl disulfide, dimethyl trisulfide and pyrimidine, which were produced under both aerobic and anaerobic conditions. Plant materials may be degraded slowly since their cellulose and lignin contents are high (Richard, 1996). In the current study, marker compounds were not produced or produced under method detection limits by plant materials. Method detection limits of dimethyl disulfide, dimethyl trisulfide, and pyrimidine were 1.10, 5.50 and 0.011 ppbv, respectively (Akdeniz et al., 2009).

In addition to swine composts, the marker compounds were also detected from additional test units (both aerobic and anaerobic) where plant and animal materials were layered and composted together at the ratio of 1 (animal):15 (plant) (w/w). In this study,

only corn silage, which contained the most complex matrix of VOC emissions (Akdeniz et al., 2007a), was used to test the production of marker compounds when plant materials were layered with swine tissues.

The presence of sulfur-containing VOCs as marker compounds of swine tissue decay is reasonable. Sulfur makes up about 0.15 % of a swine tissue mass (Shurson et al., 1998) and it is widely distributed throughout the body since sulfur-containing amino acids (e.g., methionine, cystine, and cysteine) are components of almost all proteins (0.6 to 0.8 % of a protein) (Shurson et al., 1998). Dimethyl disulfide and dimethyl trisulfide are produced by microbial decomposition of sulfur-containing amino acids under aerobic and anaerobic conditions. This process likely entails the sequential steps of the breakdown of protein to form peptides and degradation of the peptides to form free sulfur-containing amino acids. It has been shown that sulfur-containing amino acids are broken down to form methyl mercaptan, dimethyl disulfide and dimethyl trisulfide by oxidation and enzymatic activity (Kadota and Ishida, 1972; Shurson et al., 1998; Higgins et al, 2002; Tulio et al., 2003). In this study, methyl mercaptan was not detected from decaying swine tissues. Pyrimidine is a heterocyclic aromatic organic compound similar to pyrazine, containing two N atoms at positions 1 and 3 of the six-member ring. No information has been found about possible processes responsible for the production of pyrimidine.

3.3 Quantification of marker VOCs

Extraction temperatures for SPME were compared according to the amount of analytes extracted at 1 hr sampling time. The highest extraction efficiency was achieved at 20 °C (Fig. 3). As the temperature increased, the extraction efficiency decreased due to the

exothermic nature of the adsorption process. The amount of analytes extracted at 20, 30, and 40 °C were found to be significantly higher than those extracted at 50 °C and 60 °C (Fig. 3). For this reason, calibration curves were prepared at 20, 30, 40, 50, and 60 °C (Table 2). The replicates exhibited relative standard deviations ranging from 0.22 to 6.15 % and correlation coefficients ranging from 94.7 to 99.7 %. The lowest and highest concentrations prepared for the calibration curves were 0.01 ppmv and 6.85 ppmv, respectively. Concentrations and emission rates of the marker compounds were estimated using these calibration curves.

3.4 Concentrations and emission rates of marker VOCs

Measured concentrations of the marker compounds ranged from below method detection limits (MDLs) to 36.86 ppbv for dimethyl disulfide, 31.66 ppbv for dimethyl trisulfide, and 2.40 ppbv for pyrimidine under aerobic conditions. Under anaerobic conditions, measured concentrations ranged from below MDLs to 59.04 ppbv for dimethyl disulfide, 62.01 ppbv for dimethyl trisulfide, and 10.46 ppbv for pyrimidine. The relative standard deviation (RSD) range of measured concentrations from triplicate units was 2.37 to 10.0 %. The MDLs for these marker compounds in gas phase were reported as 1.10, 5.50 and 0.011 ppbv for dimethyl disulfide, dimethyl trisulfide, and pyrimidine, respectively (Akdeniz et al., 2009).

Estimates of emission rates of the marker VOCs from aerobic and anaerobic test units are shown in Figs. 4a and b. In these figures, emission rates were reported for the whole mass of the compost material at the time of measurement. Marker compounds were not detected in the 1st week (sampled on the 2nd day) of the process. In the 2nd week (9th day)

of the process, marker compounds were found to be in the headspace of the test units. The highest emission rates were measured in the 3rd week of the process. In this week, under aerobic conditions, the emission rates were 1.24×10^{-2} , 1.43×10^{-2} , and 6.80×10^{-4} $\mu\text{g}/\text{min}$ for dimethyl disulfide, dimethyl trisulfide, and pyrimidine, respectively. At anaerobic conditions the emission rates were 3.93×10^{-5} , 5.53×10^{-5} , and 5.93×10^{-6} $\mu\text{g}/\text{min}$ for dimethyl disulfide, dimethyl trisulfide, and pyrimidine, respectively. After the 3rd week, emission rates significantly decreased. After the 6th week, marker compounds were not detected from the headspace of the test units. In week 6, concentrations of the marker compounds in the headspace were lower than the MDLs and the available sources of marker emissions were most likely depleted. Under aerobic conditions, the emission rates were estimated to be below 0.51×10^{-4} , 3.43×10^{-4} , and 4.35×10^{-7} $\mu\text{g}/\text{min}/(\text{final g VS of swine tissue})$ for dimethyl disulfide, dimethyl trisulfide, and pyrimidine, respectively. At anaerobic conditions the emission rates were 0.37×10^{-7} , 2.51×10^{-7} and 3.19×10^{-10} $\mu\text{g}/\text{min}/(\text{final g VS of swine tissue})$ for dimethyl disulfide, dimethyl trisulfide, and pyrimidine, respectively. These emission rates were calculated based on MDLs, final g VS of swine tissues and compost temperature in week 6. Emission rates were reported per final g VS (VS of compost materials after 9 weeks) to facilitate comparisons between the results of this lab-scale study and larger scale composting studies.

Temperatures of the test units were purposefully raised at the end of the composting process (week 8) (Fig. 2). This increase in temperature did not result in increased emission rates of the marker compounds and marker compounds were not detected in the headspace (Figs. 4a and b). This indicated that the emission rates of the marker compounds did not decrease due to a lower temperature and volatility. It is most likely that available nutrient

sources were depleted and microbial degradation process was completed. These results were supported by the respiration rate measurements. Respiration rates of the swine tissues decreased from 8.82 ± 0.36 to 3.25 ± 0.12 mg CO₂-C/g VS/d (Table 3). Thompson (2002) classified compost materials with respiration rates below 5 mg CO₂-C/g VS/d as stable composts.

Emission rates of marker VOCs were much higher under aerobic conditions compared to anaerobic conditions. During the period where emission rates were apparently highest (Figs. 4a and b), emission rate of dimethyl disulfide under aerobic conditions was 12.39×10^{-3} µg/min compared to 3.92×10^{-5} µg/min under anaerobic conditions. This represents an approximately 200-fold difference. The higher emission rates of dimethyl disulfide and dimethyl trisulfide under aerobic conditions might be explained considering the production mechanism. Possibly oxidation (in aerobic conditions) of sulfur-containing amino acids to form dimethyl disulfide and dimethyl trisulfide might be faster and preferred pathway than enzymatic degradation (in anaerobic conditions) since most degradation processes occur more rapidly under aerobic conditions (Haug, 1993).

An important observation was that emissions of volatile fatty acids (VFAs) were detected from only anaerobic test units of plant materials (Table 1). These results were expected since VFAs are known to be produced during anaerobic degradation (Haug, 1993). In further field-scale biosecure composting studies, a potential use of VFAs to evaluate aeration status of compost materials could be evaluated.

Emission rates of dimethyl disulfide and dimethyl trisulfide were approximately 12 times higher than the emission rates of pyrimidine. This ratio was consistent in both aerobic

and anaerobic test units. Significant correlations (correlation coefficients ranging from 83.7 to 99.6 %) were found between emission rates of dimethyl disulfide, dimethyl trisulfide, and pyrimidine (Table 4), indicating that these organic compounds were likely produced simultaneously by microbial activity. Based on these results, emission rates of the three marker compounds can also be estimated if emission rate of one of the marker compounds is known (Table 4).

The results of this study serve as a ‘stepping stone’ to field-scale research on the degradation progress of biosecure swine mortalities. In this study, aeration rate, temperature profile, composting time, carbon to nitrogen ratio, moisture content of the compost materials were carefully chosen to simulate a field-scale biosecure composting process. The results of this study will be supported by subsequent field-scale biosecure swine mortality composting studies since there could be additional variables affecting larger-scale degradation processes.

4. Conclusions

Volatile organic compounds emitted from decaying swine and plant materials were characterized in a laboratory-scale system simulating biosecure field-scale swine mortality composting operations. The novel approach involving SPME coupled with collection of VOCs from a complex matrix of decaying plant and animal tissues, and analysis of VOCs on a GC-MS was useful in identifying marker compounds that could be used as indicators of the process status and its completion. Three marker compounds, dimethyl disulfide, dimethyl trisulfide, and pyrimidine were found to be produced only by decaying swine tissues. Marker compounds were found to be produced simultaneously and the highest

emission rates were detected during the third week of the composting process. Marker compounds were not detected after the 6th week of the process. The decrease in the emission rates of marker compounds after week 6 was not caused by change in the temperature and lower volatility of the compounds. The main reason was likely slower microbial activity due to limited nutrient sources and earlier exposure to high temperatures. Respiration rates of the swine tissues were measured at the end of the trial (week 9). Volatile fatty acids were only detected in the headspace of decaying plant materials under anaerobic conditions. Significant correlations (correlation coefficients ranging from 83.7 to 99.6 %) were found between emission rates of dimethyl disulfide, dimethyl trisulfide, and pyrimidine. Consequently, the emission rate of one of these three marker compounds could be used to estimate completion of the carcass degradation in biosecure swine mortality composting systems. Therefore, future studies to monitor completion of biosecure field-scale swine mortality compost systems using the VOCs characterized in this study are warranted.

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Figure captions

Fig. 1. Schematic of the test units and dry/wet bulb temperature measurements (only 3 of the 12 test units are shown): (a) aerobic, (b) anaerobic

Fig. 2. Temperature profile used to simulate field-scale warm season animal mortality composting process based on previous work (Ahn et al., 2007; Glanville et al., 2007).

Fig. 3. Effect of SPME extraction temperatures at 1 h air sampling time (concentrations of dimethyl disulfide=6.85 ppmv, dimethyl trisulfide=5.95 ppmv, and pyrimidine=6.25 ppmv; three measurements for each point of the calibration curves).

Fig. 4. Measured emission rates of dimethyl disulfide, dimethyl trisulfide, and pyrimidine from swine tissue composting test units (from triplicate model compost units): (a) aerobic, (b) anaerobic